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Mechanism of GEMS formation

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ABSTRACT

GEMS (glass with embedded metal and sulfides) in interplanetary dust particles (IDPs) were examined using 200 keV analytical transmission electron microscopy. The morphologies and crystallography of embedded relict grains reveal that GEMS are pseudomorphs formed by irradiation processing of crystals free-floating in space. Some GEMS retain a compositional and morphological “memory” of the crystal from which they formed. Pseudomorphism rules out condensation, annealing, flash heating, or shock melting as alternative mechanisms of GEMS formation. A significant and often dominant fraction of the atoms in GEMS were sputtered deposited from other grains. Therefore, a normal (solar) isotopic composition is not a reliable indicator of whether GEMS formed in the solar system or in presolar interstellar or circumstellar environments.

1. Introduction	3
2. Results	4
3. Discussion	7
4. Acknowledgment	10
6. References	11
6. Figure captions	14

1. Introduction

Interplanetary dust particles (IDPs) are collected in the stratosphere using NASA ER2 aircraft (Brownlee, 1985; Sandford, 1988; Warren and Zolensky, 1994). A class of submicrometer-sized grains known as GEMS (glass with embedded metal and sulfides) are major constituents of the anhydrous chondritic porous (CP) class of IDPs (Fig. 1) (Bradley, 1994; 2004). Most CP IDPs are believed to be from comets (Bradley et al., 1992; Brownlee et al. 1997). The mineralogy, physical, and optical properties of GEMS are consistent with those of interstellar “amorphous silicates” (Bradley, 1994; Bradley et al., 1999). If GEMS are indeed interstellar silicates one of the fundamental building blocks of the solar system has been found. But the hypothesis has provoked debate among meteoriticists and astronomers (Flynn, 1994; Martin, 1995), and consternation within the laboratory astrophysics community (Hoppe and Zinner, 2000; Ott, 2003). The proposal that GEMS are presolar was made without measuring their isotopic compositions. The benchmark standard for identification of a presolar origin is a non-solar isotopic composition (Bernatowicz and Zinner, 1997). The isotopic compositions of GEMS were recently measured using the latest generation ion microprobe known as “NanoSIMS” (Messenger et al., 2003). Several GEMS with non-solar oxygen isotopic compositions were identified, confirming that at least some are indeed presolar grains. GEMS with non-solar oxygen isotopic compositions may also have been found within a primitive chondritic meteorite (Mostefaoui et al., 2004), although the requisite mineralogical examination using transmission electron microscopy (TEM) has yet to be performed. Most GEMS have approximately solar isotopic compositions leading some to conclude that they formed within the solar system, and that only a small fraction are of presolar origin (Keller and Messenger, 2004a).

Bradley (1994) proposed that since GEMS formed by irradiation processing of crystalline mineral grains, isotopic composition is not a reliable method for establishing a presolar origin. During irradiation processing crystalline mineral grains become progressively amorphised and chemically homogenized, as evidenced by the glassy silicate structures and approximately chondritic (solar) bulk elemental compositions of most GEMS. Presumably isotopic compositions become similarly homogenized.

However, the assertion that GEMS formed by irradiation processing has been challenged (Keller and Messenger, 2004a,b), even though irradiation-induced compositional anomalies discovered in GEMS were subsequently reported in (solar wind) irradiated rims on lunar soil grains (Keller and McKay, 1997). Rietmeijer (2004) proposed that GEMS formed by flash heating, and Keller and Messenger (2004a &b) proposed that most GEMS formed by non-equilibrium vapor phase condensation and shock melting,

In order to clarify the mechanism of formation GEMS a detailed examination of electron-transparent thin-sections (<100 nm thick) of GEMS has been performed using 200 keV analytical TEM. Most of the studied GEMS are in IDPs that contain preserved solar flare tracks, indicating that they were not heated above ~650° C during atmospheric entry (Bradley et al., 1984). Particular attention is focused on the relationship between embedded “relict grains” and the shapes of the GEMS that contain them. Relict grains are observed in ~10% of GEMS but this is likely a lower limit because, (a) specimen tilting experiments are required to establish or rule out their presence in most GEMS and, (b) individual thin-sections sample <20% of a typical GEMS volume. Irrespective of their abundance, relict grains hold the key to understanding the mechanism of GEMS formation. The observations reported here indicate that GEMS are pseudomorphs formed by irradiation processing of free-floating, submicrometer-sized mineral grains in space. Pseudomorphism rules out annealing, vapor phase condensation, flash heating and shock melting as viable mechanisms of GEMS formation and it underscores the limitations of relying on isotopic compositions to establish or rule out a presolar origin for most GEMS.

2. Results

Figure 1 shows the mechanism of GEMS formation proposed by Bradley (1994). Crystalline mineral grains like forsteritic olivine (Mg_2SiO_4) or pyrrhotite (~FeS), functioning both as a target for radiation sputtering and a substrate for sputter deposition, transform from euhedral crystals into spheroidal GEMS. At the same time grain composition changes from that of the substrate crystal (e.g. ~FeS) to an

approximately solar (chondritic) bulk composition. All GEMS contain kamacite (FeNi metal) and pyrrhotite nano-crystals embedded within amorphous silicate matrix (Bradley, 1994; Dai et al., 2001). Amorphous rims on lunar soil grains formed by exposure to the solar wind and rims on grains irradiated in the laboratory also accumulate metallic Fe (Keller and McKay, 1997; Dukes et al., 1999). Some GEMS also contain “relict grains”, remnants of the original substrate crystals from which they formed (Figs 1b, 2, 4, 5). Pyrrhotite ($\sim\text{FeS}$) and forsterite (MgSiO_4) are the most common “relict grains”. Less common FeNi metal and enstatite (MgSiO_3) relict grains have also been observed in GEMS. The pyrrhotite in GEMS is $[\text{FeNi}]_{1-x}\text{S}$ where $0 \leq x \leq 0.1$ (Dai and Bradley, 2001).

Figure 2 shows a 200 keV brightfield image of GEMS together with corresponding energy-dispersive x-ray maps showing distributions of O, Mg, Si, S and Fe. O, Mg, and Si are uniformly distributed and closely track each other throughout the Mg-silicate glass matrices of GEMS. Fe and S track one another in pyrrhotite inclusions. Fe uncorrelated with other elements indicates Fe(Ni) metal (kamacite) inclusions. A relict metal grain is indicated in the Fe x-ray map. Spatial resolution in the maps is ~ 4 nm as indicated by the smallest Fe(Ni) metal inclusion resolved (see Fe map).

Figure 3a is a darkfield image of a relict pyrrhotite grain embedded within the glass matrix of a GEMS. The surface of the pyrrhotite crystal exhibits a distinctive nanoscale roughness or “scalloped” appearance. Figure 3b is an image of the surface of an enstatite (MgSiO_3) crystal on an outer surface of an IDP that was directly exposed to the solar wind (Bradley, 1994). Figure 3c is an image of the surface of a lunar anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) crystal (from a lunar fines extract) that was also directly exposed to the solar wind. The surfaces of both the enstatite and anorthite crystals (Figs. 3b&c), like the surface of the pyrrhotite relict grain (Fig. 3a), exhibit a “scalloped” appearance characteristic of irradiation exposure.

Figure 4a is a darkfield image of a GEMS with a relict sulfide (pyrrhotite) grain in IDP U2073B-3A. Although the relict grain is deeply eroded orthogonal crystal faces

(delineated by dotted line X') can still be recognized. A second dotted line X'', a linear expansion of X', shows that the shape of the GEMS mirrors that of the relict grain, i.e. the GEMS is pseudomorph of an originally larger ($\sim 0.3 \times 0.3 \mu\text{m}$) sulfide crystal and the relict grain is the remains of that crystal. Figure 4b is a projection of hexagonal pyrrhotite viewed along the crystallographic $[\bar{2}110]$ direction. Comparison of Figures 4a and 4b indicates that both the relict grain and the GEMS are a projection of hexagonal pyrrhotite. The surfaces of the GEMS are indexed in terms of the original pyrrhotite $(0\bar{1}10)$ and (0001) crystal faces. In other words, this GEMS retains a morphological "memory" of the crystal from which it formed.

Figure 5a is a brightfield image of a GEMS in IDP U220A19. Although the grain is significantly more rounded than the pyrrhotite-containing GEMS shown in Figure 5a, interfacial angles of $\sim 95^\circ$ and $\sim 125^\circ$ are present along the outer surface of the grain. Figure 5b is a higher-magnification darkfield image of the boxed show in (a). There is an embedded relict forsterite grain within the boxed area shown. The interfacial angles of 95° and 125° correspond to the $(\bar{1}1\bar{1})/(\bar{1}\bar{1}1)$ and $(\bar{1}\bar{1}1)/(001)$ interplanar angles of orthorhombic forsterite respectively. The adjacent $125^\circ/95^\circ$ angles are characteristic of forsterite among the minerals found in chondritic IDPs. The GEMS is a pseudomorph of the forsterite crystal and it too retains a "memory" of the size ($\sim 0.3\mu\text{m}$ diameter) and shape of the crystal from which it formed.

Figure 6a and 6b are brightfield and darkfield images respectively of a GEMS in IDPs L2009*E2 and U222B42. Although relict grains were not detected in either GEMS, shape factor and crystallographic considerations suggest that both formed from forsterite crystals (Figs. 4a–4d). Furthermore, an Mg/Si atom ratio >1 was measured at the center of one of the GEMS (Fig. 5c), confirming that a forsterite crystal was the precursor. Forsterite (Mg_2SiO_4) is the only mineral in GEMS-rich chondritic IDPs with an Mg/Si ratio >1 . Thus the GEMS shown in Figure 3c preserves both morphological *and* compositional evidence of its forsterite precursor.

3. Discussion

Shape factor and crystallographic analyses of surviving relict grains establish that GEMS are pseudomorphs of mineral crystals. Relict grains are the remnants of the original crystals from which GEMS formed. Pseudomorphic replacement associated with secondary mineralization is common in geological systems. But pseudomorphism resulting from irradiation processing has not previously been observed in nature, presumably because IDPs and their constituents are very rare examples of grains that were exposed to ionizing radiation as free-floating objects in space. In most cases extensive irradiation processing via sputtering and redeposition has transformed the structure and mineralogy of mineral crystals (forsterite, pyrrhotite, kamacite, enstatite) into glassy spheroids with homogenized compositions. Surviving relict grains can reveal direct microstructural evidence of exposure to irradiation when observed under appropriate (darkfield) imaging conditions (Fig. 3). Although it is likely that relict grains originally crystallized from the vapor phase (Bradley et al., 1983; Klöck et al., 1989), it is highly unlikely that GEMS formed by vapor phase condensation, shock melting, flash heating or annealing because none of these processes involve pseudomorphism.

Most relict grains in thin sections of GEMS are offset from their centers, which is unexpected if they were irradiated as free-floating objects in space (Figs. 1b, 2, 4, 5). There are several possible explanations for the offset. First, the position of a relict grain depends on where the section was recovered from (e.g. center vs. edge of GEMS). Second, thin-sections are typically tilted with respect to the incident electron beam to maximize the visibility of the relict grains, and the position of the relict grain can change with tilt angle. X-ray mapping is a promising new method that does not require specimen tilting to detect relict grains in GEMS (Fig. 2). However, while Fe(Ni) metal (and ~FeS) relict grains can be detected, it remains to be established whether current TEM x-ray detectors offer sufficient count rates to routinely distinguish relict Mg-silicate grains (e.g. forsterite) from the Mg-silicate glass matrices in which they are embedded. Third, surface coatings (e.g. ices) or other adhering grains may have partially shielded the otherwise free-floating GEMS from uniform irradiation in space. Finally, depending on where they formed GEMS may have been aligned relative to the irradiation source,

perhaps by magnetic alignment as superparamagnetic FeNi metal accumulated within their glassy matrices or by another as yet unidentified alignment mechanism (Jones and Spitzer, 1967; Bradley, 1994, Goodman and Whittet, 1995).

Several GEMS and forsterite crystals with non-solar oxygen isotopic compositions have been identified in IDPs (Messenger et al., 2003). This study shows that there is a genetic link between forsterite and some GEMS (Figs. 5 & 6). Presolar GEMS with anomalous oxygen isotopic compositions probably formed from forsterite crystals. It is likely that they are Mg-rich ($Mg/Si > 1$) and they may contain embedded relict forsterite crystals (e.g. Fig. 5). It has been suggested that since most GEMS have normal (solar) oxygen isotopic compositions they must have formed in the solar system (Keller and Messenger, 2004). But they could equally be presolar grains with normal oxygen isotopic compositions because either they formed from sulfide crystals (e.g. Figs. 1a, 1b, & 4) or they have long since been isotopically homogenized by prolonged exposure to irradiation processing. Before attempting to use isotopic composition to determine the solar nebula or presolar origins of GEMS it is important to first understand their mineralogy and then choose isotope measurements accordingly. It has also been suggested that since the chemical compositions of GEMS-rich IDPs are chondritic (solar), most GEMS must have formed in the solar system (Keller and Messenger, 2004a). However, the compositions of both individual GEMS and GEMS-rich IDPs differ significantly and systematically from solar abundances (Schramm et al., 1989; Westphal and Bradley, 2004).

It is indeed possible that there are two populations of GEMS, those formed within the solar system and those formed in presolar environments. But regardless of where they formed the pseudomorphic mechanism of GEMS formation means that isotopic composition is not a reliable indicator of a presolar origin. While a non-solar isotopic bulk composition unambiguously establishes that some GEMS are presolar, a solar isotopic does not unambiguously establish that most GEMS are not presolar. For GEMS formed from sulfides (Figs. 1a, 1b & 4), S isotopes offer the most potential for establishing their origins. Their Mg, Si, and O isotopic compositions likely reflect the

blending and homogenization of sputter-deposited isotopes from hundreds or even thousands of silicate grains. For GEMS formed from forsterite (Mg_2SiO_4), Mg, Si, and O isotopic compositions offer the most potential for establishing their origins, particularly if they retain relict (forsterite) grains (e.g. Fig. 5). S isotopes in forsteritic GEMS likely reflect the blending of sputter deposited isotopes from many different sulfide grains. Most GEMS may have been too extensively irradiated to retain a significant component of their original isotopic compositions.

GEMS-rich interplanetary dust particles are the most fine-grained and mineralogically complex “nanomaterials” as well as the most cosmologically informative extraterrestrial grains yet discovered. They are providing enthralling insight about grain formation, evolution, and destruction, the interaction of radiation with solids, and the exchange of atoms between the solid and gas phase in space. In February 2006 the Stardust spacecraft will return the first samples of dust collected *in-situ* at a comet (Wild-2) and hopefully contemporary interstellar dust collected in the Ulysses dust stream (Brownlee et al., 2004). The abundance of GEMS in the Stardust samples will be one of the highest priority science questions.

4. Acknowledgement

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5. References

Bernatowicz, T. J. & Zinner, E. Eds. 1997, Astrophysical implications of the laboratory study of presolar materials (AIP Conf. Proc. 402).

Bradley, J. P. 1994, *Science*, 265, 925.

Bradley, 2004, In *Treatise on Geochemistry*, Vol. 1, Meteorites, Planets, and Comets, eds. A. M. Davis, H. D. Holland & K. K. Turekian (Elsevier Pergamnon, New York) 689.

Bradley J. P. et al. 1983, *Nature*. 301, 473.

Bradley, J. P. et al., 1984, *Science*, 226, 1432.

Bradley J. P. et al. 1992, *Ap. J.* 394, 643.

Bradley J. P. et al. 1999, *Science* 285, 1716.

Brownlee, D. E. 1985, *Ann. Rev. Earth Planet. Sci.* 13, 147.

Brownlee, D. E. et al. 1997, *Lunar Planet Sci.* XXVI, 183.

Brownlee, D. E. et al. 2004, *Science* 304, 1764.

Dai, Z. R. & Bradley, J. P. 2001, *Geochim. Cosmochim. Acta* 65, 3601.

Dukes, C. A. et al. 1999, *JGR E*, 104, 1865.

Flynn, G. J. 1994, *Nature*, 371,287.

Goodman, A. A. & Whittet, D. C. B. 1995, *Ap. J.* 455, L181.

Hoppe, P. & Zinner, E. 2000, *J. Geophys. Res.* 105, 10,371.

Jones, R. V. & Spitzer, L. Jr., 1967, *Ap. J.* 147, 943.

Keller, L. P. & Messenger, S. 2004a, *Lunar Planet. Sci.* XXXV, Abs #1985.

Keller, L. P. & Messenger, S. 2004b, 67th Ann. Met. Soc. Mtg. Abs. 5186.

Keller, L. P. & McKay, D. S., 1997, *Geochim. Cosmochim. Acta* 61, 2331.

Klöck, W. et al. 1989, *Nature* 339, 126.

Martin, P. G. 1995 *Ap. J.* 445, L63.

Messenger, S. et al. 2003 *Science*, 300, 105.

Mostefaoui, S. et al. 2004, *Lunar Planet. Sci.* XXXV, Abs # 1593.

Ott, U. 2003, in *Astromineralogy*, ed. Th. Henning (Berlin; Springer) 236.

Rietmeijer, F. J. M. 2004, *Lunar Planet. Sci.* XXXV, Abs # 1060.

Sandford, S. A. 1988, *Fund. Cosmic. Phys.* 12, 1.

Schramm, L. S. et al., 1989, *Meteoritics* 24, 99.

Warren, J. L. & Zolensky, M. E. 1994, in *AIP Conf. Proc.* 310, *Analysis of Interplanetary Dust*, eds M. E. Zolensky, T. L. Wilson, F. J. M. Rietmeijer & G. J. Flynn (AIP, New York), 245.

Westphal, A. J. & Bradley, J. P. 2004 Ap. J. (submitted).

6. Figure Captions

Figure 1. The transformation from single-mineral crystal to GEMS. Brightfield electron micrographs of irradiated grains within the matrices of chondritic IDPs. Relative irradiation dose increased from (a) to (d). (a) Pyrrhotite (FeS) crystal with etched surfaces in IDP U219C2. (b) GEMS containing a deeply eroded relict FeS crystal (U2012C-2I) (c) & (d) GEMS with progressively higher irradiation doses (U220A19). (Stars in (c) and (d) indicate positions where compositions were measured using a nanoprobe (see Bradley, 1994)).

Figure 2. 200 keV brightfield image of GEMS (upper left) with corresponding x-ray energy-dispersive maps showing distributions of O, Mg, Si, S and Fe. The maps were obtained using the O-K (0.52 keV), Mg-K (1.25 keV), S-K (2.31 keV), and Fe-K (6.40 keV) x-ray lines.

Figure 3. Darkfield images of the surfaces of irradiated grains. (a) Relict pyrrhotite grain within a GEMS in IDP U219C2. (b) Enstatite grain on outer surface of IDP W7027C2. (c) Lunar soil anorthite grain (image courtesy of L. Keller). The scalloped surfaces of the grains are a fingerprint of irradiation exposure. Linear features in the enstatite and anorthite crystals (b & c) are solar flare tracks.

Figure 4. (a) Darkfield micrograph of a GEMS with an embedded relict pyrrhotite (FeS) crystal. Dotted line X' delineates the approximate shape of the relict crystal, and X'' delineates the shape of the GEMS. Comparison of X' and X'' indicates that the GEMS is a pseudomorph of a pyrrhotite crystal. (b) Projection of the hexagonal $D_{6h} - 6/mmm$ pyrrhotite crystal structure viewed approximately parallel to $[\bar{2}110]$.

Figure 5. (a) Brightfield micrograph of a GEMS in IDP U220A19. (b) Darkfield micrograph of boxed area in (a) containing a "relict" forsterite crystal displaying adjacent interfacial angles of $95^\circ (\bar{1}\bar{1}1)/(\bar{1}1\bar{1})$ and $125^\circ (001)/(\bar{1}\bar{1}1)$. Comparison of (a) and (b)

indicates that the GEMS is a pseudomorph of a forsterite crystal and the relict grain is the remains of that crystal.

Figure 6. (a) Brightfield micrograph of a GEMS embedded in carbonaceous material ("C") in IDP L2009*E2. Dotted line delineates the shape of the GEMS. (b) Projection of the orthorhombic $D_2 - 222$ forsterite crystal structure viewed approximately parallel to $[0\bar{1}\bar{1}]$. Comparison of (a) and (b) indicates that the GEMS is a pseudomorph of a forsterite crystal. (c) Darkfield micrograph of a GEMS in IDP U222B42. Dotted line delineates the shape of the GEMS. (d) Projection of the forsterite D_{2h} -mmm crystal structure viewed approximately parallel to $[100]$. Comparison of (c) and (d) indicates that the GEMS is a pseudomorph of a forsterite crystal.

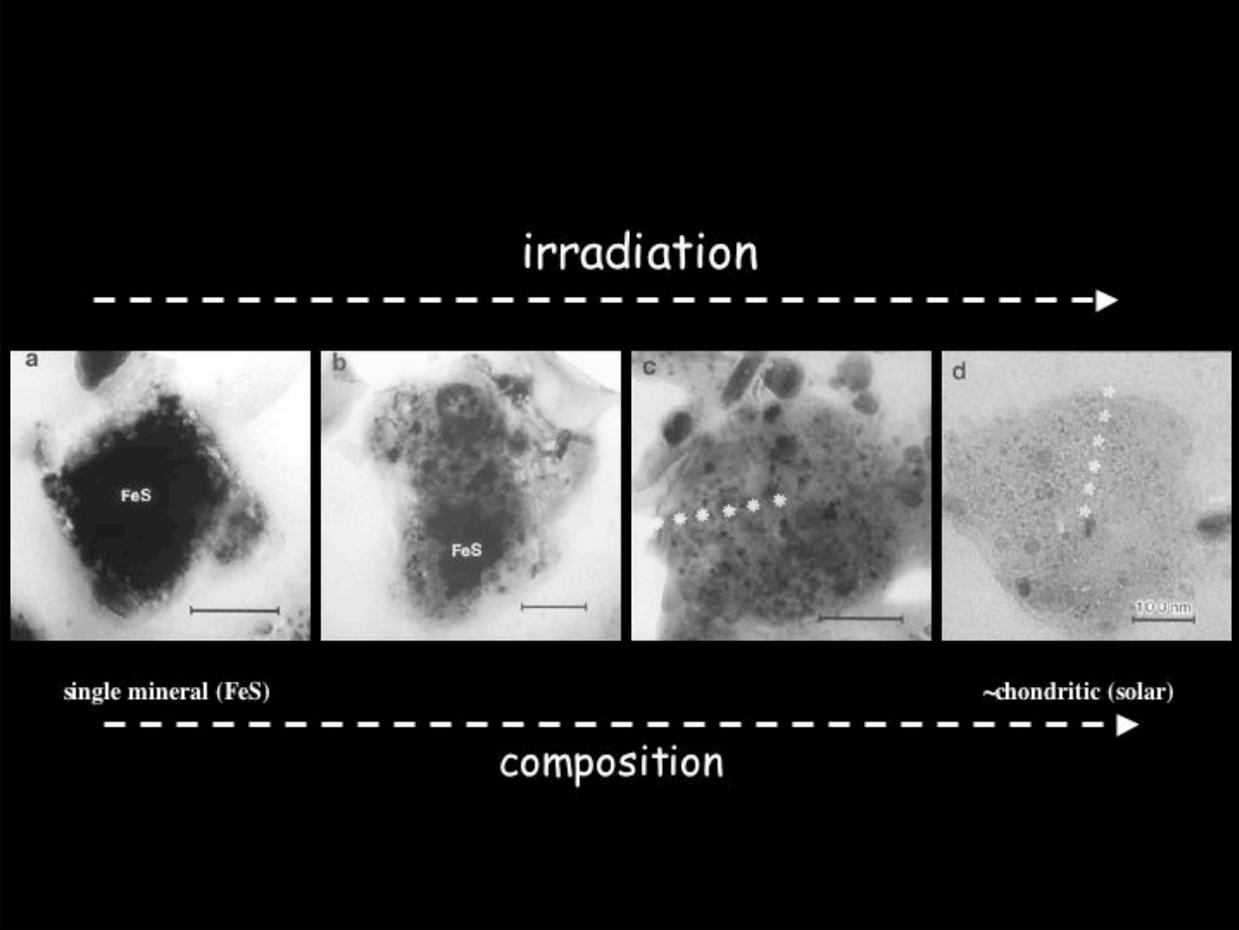


Figure 1

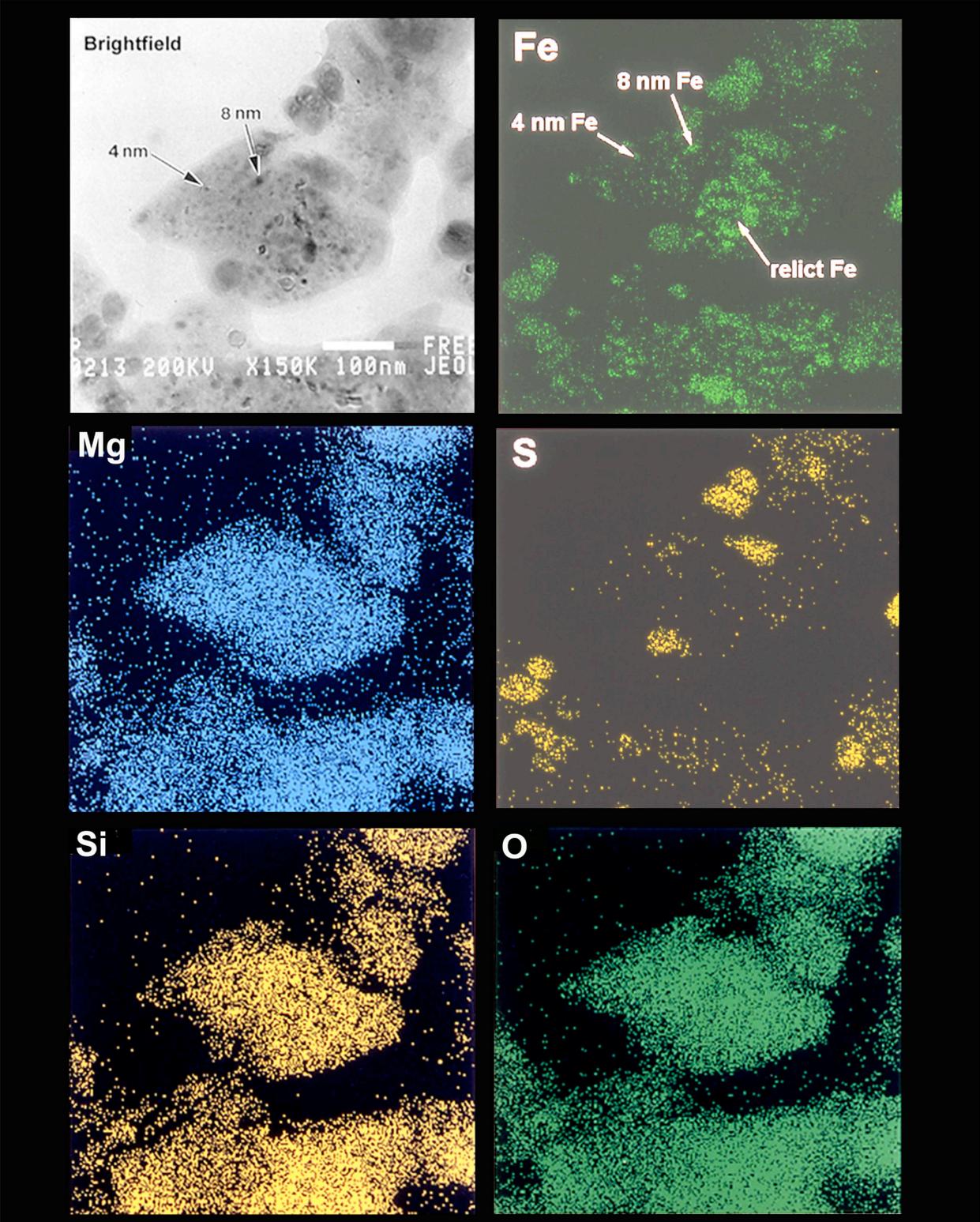


Figure 2

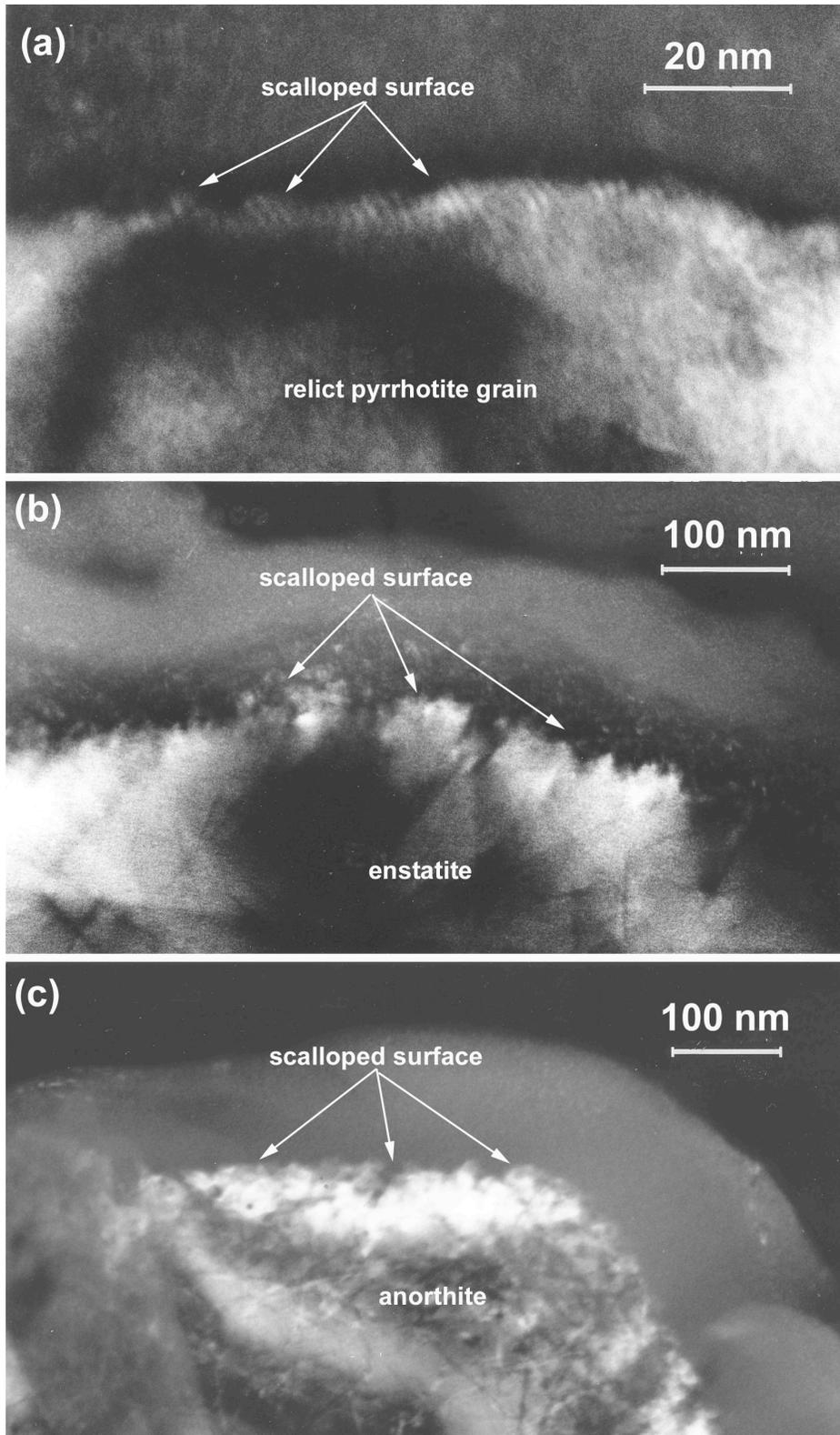


Figure 3

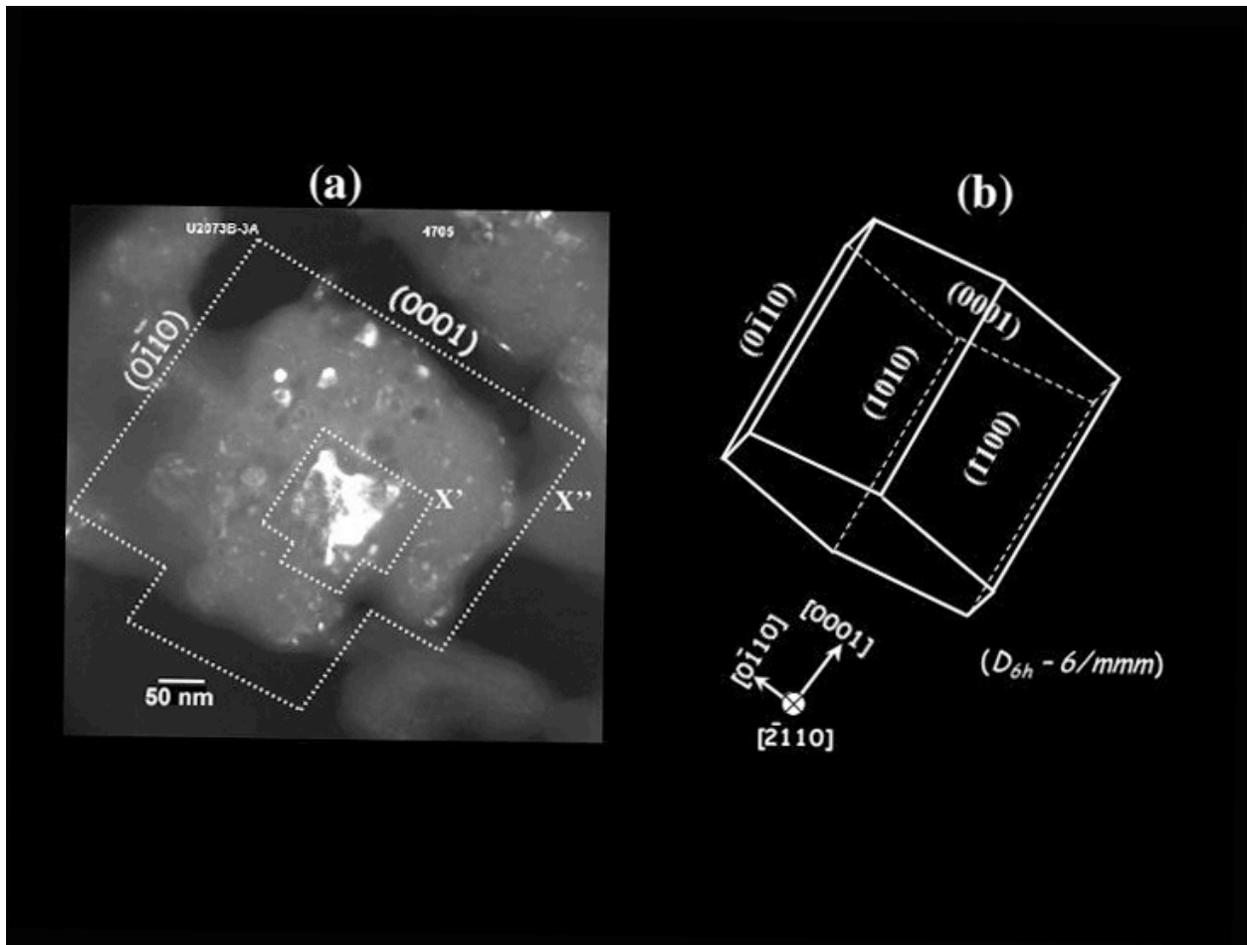


Figure 4

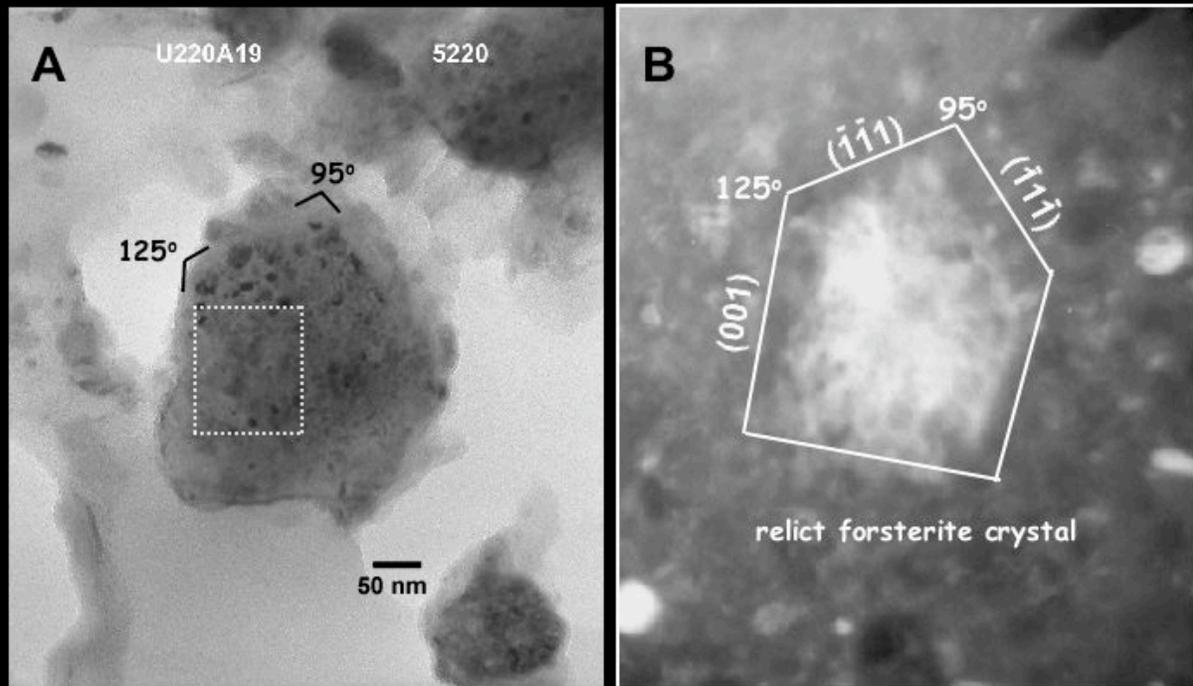


Figure 5

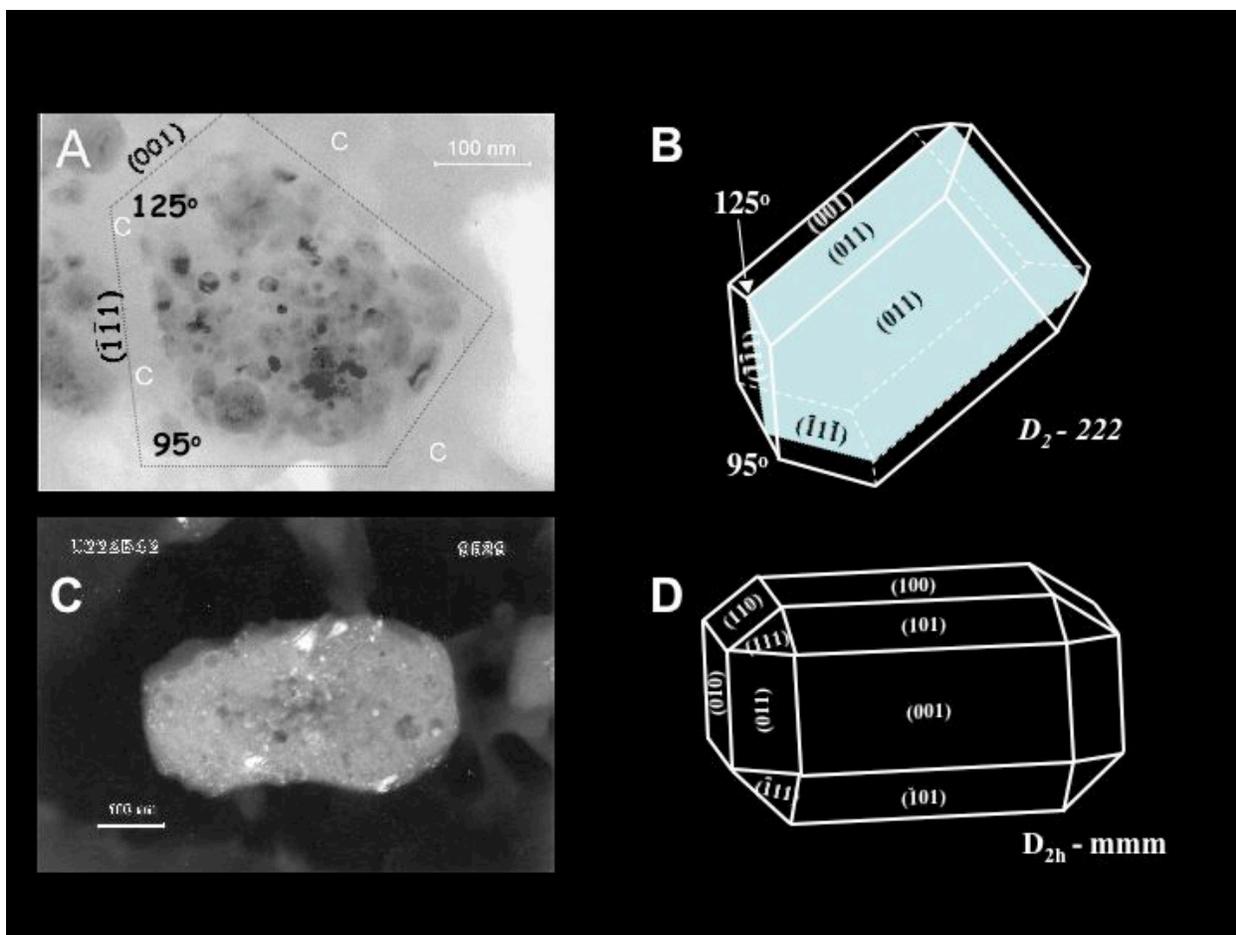


Figure 6